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(54) Thin film detector of ultraviolet radiation, with high spectral selectivity option

(57) Thin film detector of ultraviolet radiation, with high spectral selectivity option, consisting of a structure placed between two electrodes, formed by the superposition of semiconductor thin films such as hydrogenated amorphous silicon and its alloys with carbon. The device is able to absorb a large quantity of UV radiation and to convert it into electric current being transpasrent to photons of longer wavelenghts. Its deposition technique allows fabrication on substrates of glass, plastic, metal, ceramic types of materials (also opaque, also flexible), on which a conductor material film has been pre-deposited. It can be fabricated on substrates of any size. Its field of application concerns: - detection systems operating in the ultraviolet spectrum and/or one or two additional band functioning in other spectral regions; - ultraviolet radiation detection systems with high rejection of radiation at greater wavelengths. For example, it finds advantageous applications in the area of laboratory spectroscopy, clinical diagnostics, clinical analyses, astrophysics, astronomy, and other applications.

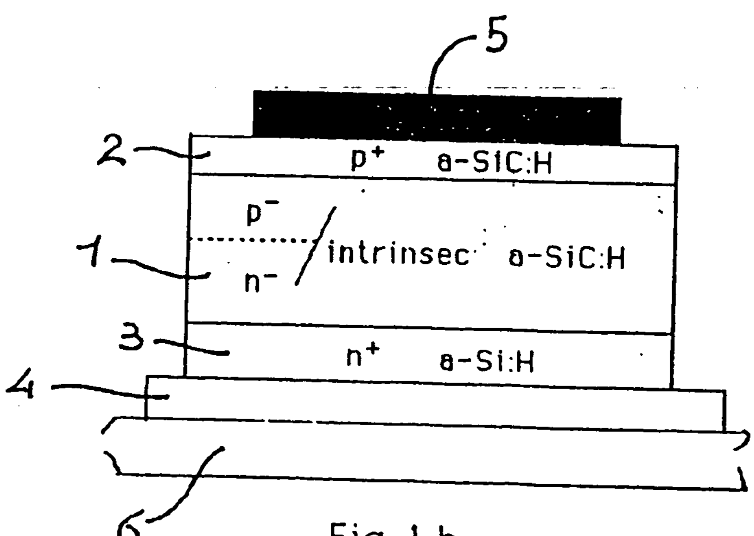

Fig. 1 b

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Description

This invention concerns a sensor that permits detection of ultraviolet light (UV, with λ <400 nm wavelength) with high rejection of radiation at longer wavelengths.

The photodetector presented herein consists of a p^+-n^+ junction in hydrogenated amorphous silicon-carbon alloy (a-SiC:H) between two electrodes connected with the exterior and is fabricated with the well-known technologies for thin films. The temperatures during the whole fabrication process are such that it can be realized on any substrate: glass, plastic, metal. Thanks to the technologies used, fabrication is possible under the form of large-area, high resolution two-dimensional matrixes.

The invention in question lies in the field of UV radiation detection and finds application in the case of detection of ultraviolet components of the light on an unwanted background of visible and/or infrared radiation to be filtered, in which a high spatial resolution of the two-dimensional image is necessary.

The invention can be used to detect phenomena accompanied by emission of light; for example, instrumentations for detection of astronomic and astrophysical data; instrumentations for control of reactions in chemical and biological fields; ionized gases spectroscopy (fusion plasmas and electric shock plasmas; clinical diagnostics, etc.).

It can be employed in the development of:

- detection systems with one window functioning in the ultraviolet spectrum and with one or two additional windows functioning in other spectral regions;
- ultraviolet radiation detection systems with high rejection of radiation at longer wavelength;
- large-area, high-resolution matrix systems of detection in the ultraviolet spectral range.

The real focal point of the invention lies in the possibility to absorb a large quantity of ultraviolet radiation and to convert it into electric current letting, instead, the photons of other spectral ranges pass unhindered. In this invention the UV light absorption is made possible by the following factors:

- the frontal electrode is a metal grid which offers to the incident light open areas through which the light can pass;
- the UV that passes through these open areas is absorbed in the p^+ layer and converted into electric charge carriers;
- the electrons photogenerated in the p^+ can reach the rear electrode, crossing the entire structure.

Selectivity in the ultraviolet is possible if the thickness of the detector is much below the dimension on which there is a strong absorption of the visible and infrared radiation.

Currently some types of highly sensitive ultraviolet light photodetectors are commercially available. We shall divide these UV detectors into two categories: (a) single-channel detectors, for a punctual detection, and (b) multi-channel detectors, for a two-dimensional detection. The single-channel detectors include: the photomultiplier tubes and the crystalline silicon photodiodes. Multi-channel detectors are: the crystalline silicon photodiode arrays, the charge-coupled devices (CCD) and the multi-channel plates (MCP). The well-known photomultiplier tubes permit the detection of ultraviolet radiation with high sensitivity and selectivity with respect to the visible, by appropriately selecting the cathode material. However, the use of photomultipliers has a number of disadvantages which are overcome by the invention in question. In fact, photomultipliers require typical power supply voltages exceeding one thousand volts: they are vacuum tubes, difficult to handle, bulky, and which do not allow the integration of several elements.

Crystalline silicon photodiodes have an optimum efficiency in the visible spectral range but can allow the detection of ultraviolet radiation only after sophisticated and expensive mechanical and optical treatments. They require low power supply voltages and can be integrated in arrays of a few centimeters size.

Concerning the UV-CCDs, they are crystalline silicon components for which are necessary very special treatments, as well. They are multi-channel detectors which are highly sensitive, with high signal/noise (S/N) ratios, especially if they work at low temperatures. Basically ccDs are analog, linear shift registers: the electrons photogenerated within the silicon are collected in a matrix of pixels which are then read sequentially; the two-dimensional image can thus be reconstructed. But, at least three major disadvantages exist for detection of ultraviolet radiation by CCDs : the cost, the impossibility to provide large-area two-dimensional matrixes, and the necessity to filter the visible radiation in the case that ultraviolet components on another radiation background must be detected.

The Micro-Channel Plates (MCP) amplify even very weak light signals, through a cascade multiplication process. They consist of millions of microscopic conductive glass tubes fused together in a disc-form base, to the heads of which is applied a high potential difference (typically of 1,000 V). The MCPs can function as image intensifiers or as photon counters and, thus, have an excellent sensitivity. They are treated at the input stage, with the deposition of a selective sensitivity photocathode, and at the output stage, with a phosphorous shield. Due to their high sensitivity and S/N ratio performances, MCPS are used in space applications and in astrophysics. However, the wide commercialization of MCPs en-

counters difficulty because of their high costs due to the technological complication and the 1,000 V power supply.

With respect to the commercial UV photodetectors, the invention solves the problems of: filtering of the background visible and infrared radiation; electric power consumption; large areas integration, and, in addition, is less costly.

With the invention presented herein the optimization of the thicknesses and coefficients of absorption of the amorphous semiconductor layers composing the junction, as well as of the geometry of the metal grid that serves as frontal electrode is performed. Besides increasing the maximum detection efficiency in the UV, this optimization allows also tuning of the operating band of the detector by shifting it toward the near UV radiation or toward the far UV radiation, depending on the applications. In fact, it had already been demonstrated by other researchers that, by acting on the deposition parameters and on the type and concentration of impurities in the eventual alloy with silicon, absorption could be enhanced in the visible range toward the UV or toward the infrared radiation. Thus the physical parameters to be optimized are: (a) the absorption profile and (b) the thickness of the detector. This optimization can be obtained by the control of the deposition parameters among which, according to the inventors:

- the deposition time
- the percentage of carbon in the alloy.

The optimization and the reproducibility of the thicknesses of the layers is made possible by control of the Glow Discharge time of deposition, the other parameters being fixed. The coefficients of absorption of the hydrogenated amorphous silicon alloy ,instead, depend upon the fundamental properties of the material such as, the extension of the energy and optical gap of the semiconductor and the density of the defect states in the gap. These, in turn, depend upon the growth parameters in a very complicated way. A simple and repeatable method for varying the absorption coefficient profile as a function of the wavelength is to form silicon/carbon or silicon/germanium alloys in known percentages. This is obtained through the introduction of a controlled flow, respectively, of methane or germanium gas in the deposition chamber. The resultant carbon/silicon alloy is an amorphous semiconductor of a greater energy gap than the amorphous silicon, which penalizes the absorption of the visible and of the infrared with respect to the ultraviolet radiation.

However, the a-SiC alloy to be used in the device in question must not contain too high percentages of carbon with respect to silicon, because its electronic properties would prove poor.

The invention is now described on the basis of a version currently preferred by the Inventors and making reference to the following Figures, enclosed:

Fig. 1: Physical structure of the invention:

- view from above (1a) depicting the metal grid (5) and the transparent element (6) (glass, quartz, etc.)
- cross section (1b) depicting: the thin semiconductor layers (1, 2 and 3), the transparent conductor (4), the metal grid (5) and the glass (or quartz) (6).

Fig. 2: Schematization of the profile of the light intensities within the device for three sample wavelengths.

Fig. 3: Schematic representation of the expected quantum efficiency curve in case of high selectivity .

Fig. 4: Schematic representation of the expected quantum efficiency curve in case of high sensitivity also in the visible.

In Fig. 1 is shown the need for an intermediate layer between two p^+ and n^+ amorphous silicon doped layers, for the purpose of forming the rectifying junction. This intermediate layer must be very slightly defected; this is obtained, for example, by using low doping or undoped (intrinsic) layer so as to form, respectively, a p^+-p^--n^--n^+ or a p^+-i-n^+ structure. In the case of the p^+-i-n^+ detector, the application of a reverse polarization may not be effective, because the junction would be crossed by a significant dark current due to microscopic short circuits which would penalize the relationship between photocurrent and dark noise. The presence of a significant inverse saturation current is typical of very thin and defected p-i-n- diodes in a-Si:H. From these considerations, a better operation of the device in question is to be expected in terms of S/N ratio, with polarization voltages around zero.

concerning Figure 1b, it must be borne in mind that the real dimensions of the layers will be qualitatively discussed in the patent text. In the drawing the relationships between dimensions are not maintained due to graphics reasons.

In observing Figure 1a, it is noted that the electromagnetic radiation penetrates into the amorphous device through the open regions of the metal grid and crosses serially layers (Fig. 1b): p^+ of a-SiC:H; intrinsic or p^-/n^- of a-SiC:H; n^+ of a-Si:H. The order of the various layers composing the device is reversible in case of use of a substrate transparent to the UV light, such as quartz, magnesium fluoride or the like. In this case, the structure becomes: substrate, metal grid, p^+-n^+ junction with the previously described intermediate layer, rear electrode.

However, the first active layer is the p^+ layer (which we will call window layer). Based on the typical values

of the absorption coefficients provided in literature it is found that, in a p^+ of a-SiC:H with 50% percentage of carbon, all the ultraviolet radiation is absorbed essentially in the first 5 nm (Fig. 2). This dimension is of the same order as the diffusion length of the electrons (minority carriers) in that material. Hence, by dimensioning the thickness of the p^+ layer around this value a good probability is anticipated for collection of the electron-hole pairs photogenerated in the p^+ layer after the absorption of the UV. Thinner thickness of the p^+ layer is technologically inadvisable as it worsens the quality of the junction, whereas greater a-SiC:H thicknesses would penalize collection of carriers and, consequently, the photocurrent. Greater thicknesses could be considered of the p^+ layer of an a-SiC:H alloy less rich in carbon could be considered, since the diffusion length is greater; in this case the transparency to the visible would be less (and selectivity as well).

The high value of energy gap of the p^+ layer (also exceeding 2 ev) enhances transmission of the visible radiation which, thus, is negligibly absorbed in the p^+ layer.

The holes photogenerated in the p^+ by the UV light are collected by the metal grid electrode. The electrons photogenerated in the p^+ layer diffuse and reach the n^+ layer, where they are the majority carriers and, thus, are collected by the rear electrode. In the intermediate layer the electrons move by effect of the external voltage or of the contact potential, having specified that this photodetector may or may not be polarized, depending on the structure chosen.

By fixing the thickness of the intermediate a-SiC:H layer on the order of some tens of nanometers the, collection probability is high. The visible radiation is absorbed in the intermediate region in an amount that increases with increase in thickness. With the thickness of some tens of nanometers a significant absorption is obtained of the portion of the visible spectrum adjacent to the ultraviolet radiation i.e., of the blue (while the red would be so weakly absorbed as to cross almost unhindered the a-SiC:H intermediate layer, arrive in layer n^+ and escape through the transparent electrode and substrate).

The situation is schematically represented in Fig. 2.

The use of an intermediate layer in a-SiC:H decreases the absorption of the visible radiation and contributes to the selectivity of the detector, respect to the case of an a-Si:H intermediate layer.

In the thick n^+ layer of a-Si:H the collection of photogenerated carriers is an event of negligible probability.

In other words, selectivity in the ultraviolet band is ensured by the following factors:

- transparency of the p^+ layer to the visible light (a-SiC:H)
- low absorption profile in the visible also in the intermediate layer (a-SiC:H)
- small thickness of the intermediate layer.

The high quantum efficiency in the ultraviolet radiation is ensured by the relationship between open area and opaque area in the metal grid, and between thickness of the p^+ layer and length of diffusion of electrons.

From what has been said, a maximum sensitivity of the detector is obtained in the ultraviolet radiation, which progressively decreases with the increase in wavelength, i.e. from the blue toward the red, with insignificant efficiency values in the infrared.

Let us clarify the meaning of maximum sensitivity in ultraviolet radiation. In principle, if the diffusion length in the p^+ layer was much greater than its thickness, all the carriers photogenerated in the p^+ would have a high probability of contributing to the photocurrent, also those generated in the mere surface.

However, this is not the case, since from literature it is known that the diffusion lenght of electrons in that material does not exceed a few nanometers. Thus, the sensitivity should decrease with wavelenght on the far UV range. Another mechanism takes place, which increases the collection probability of photocarriers with decreasing wavelenght: the electron yield effect. This effect gives rise to the generation of more than one electron-hole couple after absorption of one photon, if the photon energy largely exceeds the energy gap of semiconductor. For example, photons with wavelenght below 300 nm have energies greater than two times the energy gap of the a-SiC:H used in p^+ layer, and can contribute to a multiple photogeneration mechanism. considering all the effects mentioned above the sensitivity of the photodetector should remain constant over all the UV band, also in the far-ultraviolet radiation and beyond.

Fig. 3 shows inhicatively the expected quantum efficiency curve in arbitrary units for a structure like that shown in Fig. 1, calculated on the basis of the absorption relative to the various wavelengths and of the typical values provided in literature of the transport constants of the semiconductors under study.

With this invention it is possible to produce also a photodetector with high spectral response in the UV and also in the visible region (i.e. of the type schematically represented in Fig. 4). In this case the structure is the following: p^+-i-n^+, modified according to the following criteria:

- an intrinsic layer is deposited in a-Si:H instead of a-SiC:H, to increase absorption of the visible;
- its thickness is increased up to a few hundreds of nanometers, as is used in a-Si:H solar cells, where it is intended to absorb the visible;
- a metal rear electrode is applied, to reflect the still unabsorbed radiation and cause it to pass again in the active layer.

The deposition technique used for the photodetector permits fabrication on glass, plastic, metal and ceramic types of substrates (also opaque and flexibile) on which a conductor material film has been pre-deposited. In addition, said technique allows fabrication in any area, even very large area surfaces, if the deposition machine is set for large area work. Thus, by utilizing the concepts just expressed, large-area, two-dimensional matrixes can be fabricated of said photodetectors (pixels), whose minimum dimension depends on external factors (the lithographic technique in use) and determines the spatial resolution. To this is added the fact that the thicknesses and profiles of absorption of the layers can be optimized so as to make the window functioning in the ultraviolet spectrum very selective. Furthermore, if the rear electrode and the substrate are transparent to the visible, a large part of the transmitted radiation can finally exit from the detector through them enhancing selectivity. Said thicknesses and profiles of absorption of the layers can be optimized so as to extend the operation of the detector to the visible. As mentioned earlier, to further increase the efficiency of detection in the visible, a metal rear electrode can be used, which reflects radiation , making it to pass through the intrinsic layer for the second time.

The present structure can be lengthened to a back-to-back diode structure (of the type: p^+-i-n^+-i-p^+), still composed of thin films of hydrogenated amorphous silicon and its alloys such that they present a second operation band in another spectral range. The back-to-back diode photodetector presents a second operation band at longer wavelengths , which can be in the infrared region if the second added diode is made of hydrogenated amorphous silicon-germanium alloy. The photodetector diode structure can be further lengthened to a p^+-i-n^+-i-n^+-i-p^+ structure (according to the information of applic. No. RM94A 000294), also composed of thin films of hydrogenated amorphous silicon and its alloys, which has a second and third operation bands centered at longer wavelengths, under the polarization conditions explained in the above-mentioned patent.

Claims

1. Photodetector with spectral band operating in the ultraviolet region (Fig.1b),characterized by the fact that it is a structure composed of an overlaying of semiconductor thin films, preferably of hydrogenated amorphous silicon (3) and its alloys with carbon (1)(2), placed between two electrodes (4), (5) and deposited on a substrate (6).

2. A photodetector according to Claim 1, characterized by the fact that its structure forms a p^+n^+ rectifying junction (2), (3) in a-SiC:H/a-Si:H.

3. A photodetector according to Claim 1, characterized by the fact that the diode structure can be lengthened to a back-to-back diode structure, again made up of thin films of hydrogenated amorphous silicon and its alloys such as to present a second band functioning in another spectral range.

4. A photodetector according to claim 3, characterized by the fact that it presents a second band functioning at longer wavelengths , as in the infrared range if the second added diode is made up of hydrogenated amorphous silicon-germanium alloy.

5. A photodetector according to Claim 1, characterized by the fact that the diode structure can be lengthened to a p^+-i-n^+-i-n^+-i-p^+ structure (according to the information of applic. No. RM 94A000294), also consisting in thin films of hydrogenated amorphous silicon and its alloys which presents a second and third spectral window centered at longer wavelengths, under the polarization conditions explained in the above-mentioned patent.

6. A photodetector according to claim 1, characterized by the fact that it can be fabricated in different materials, provided that they satisfy the desired functional characteristics.

7. A photodetector according to the previous Claims, characterized by the fact that it can be employed in the fabrication of large-area, high-resolution matrix for UV detection systems.

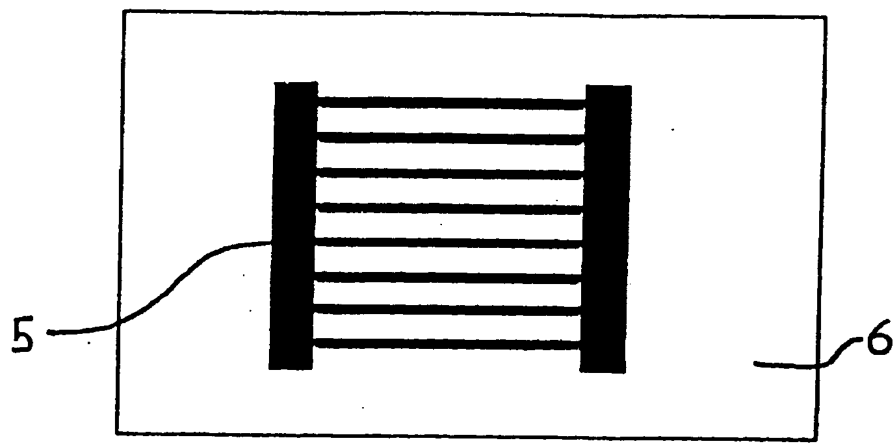


Fig. 1 a

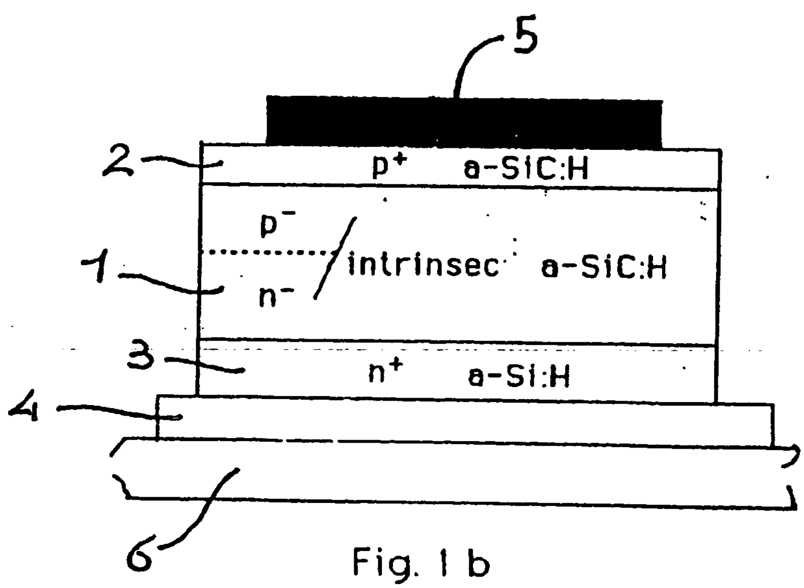
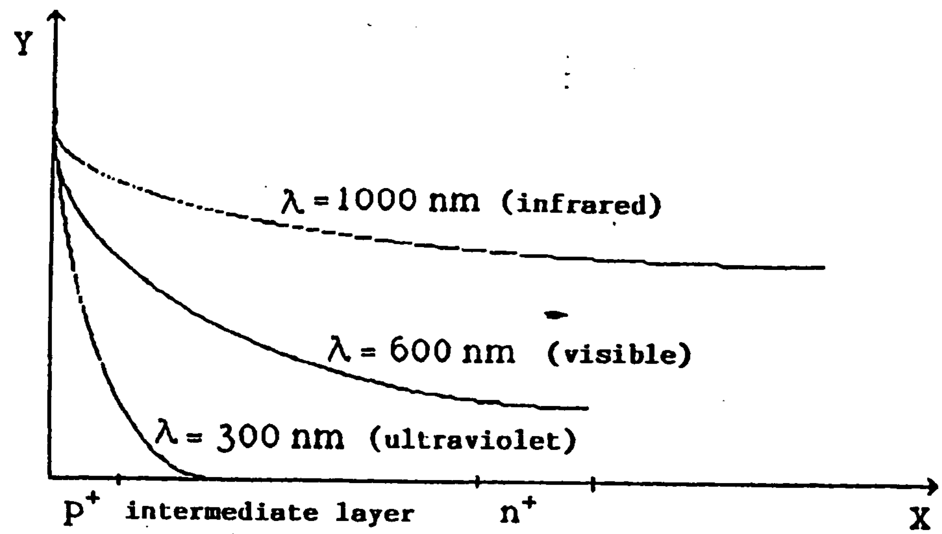
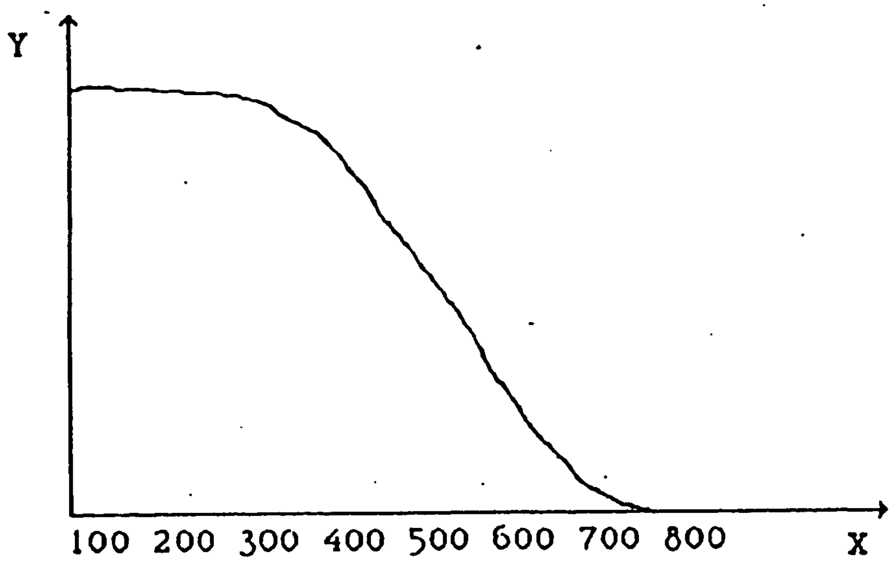


Fig. 1 b



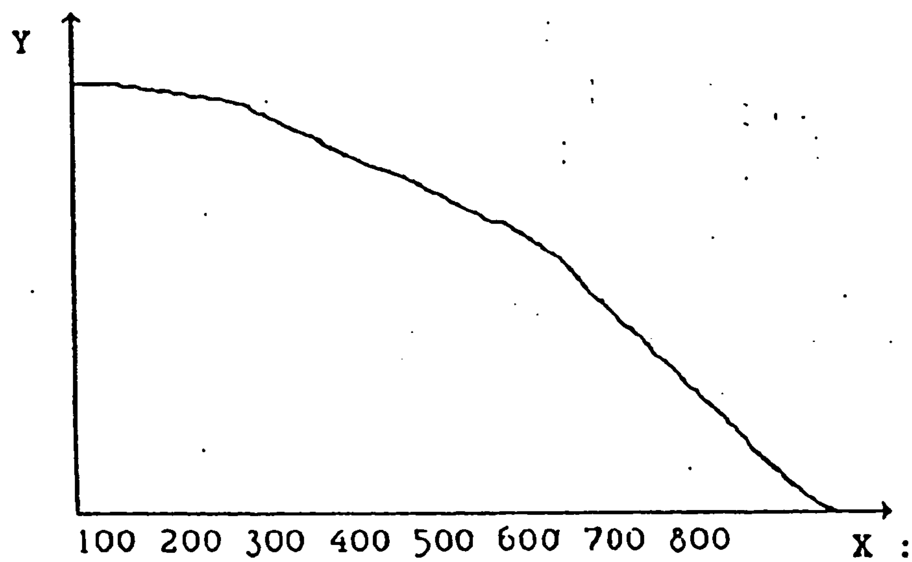
X- distance from the surface exposed to radiation
Y- intensity of the light in the detector

Fig. 2



X- radiation wavelength
Y- quantum efficiency

Fig. 3



X- radiation wavelength
Y- quantum efficiency

Fig. 4

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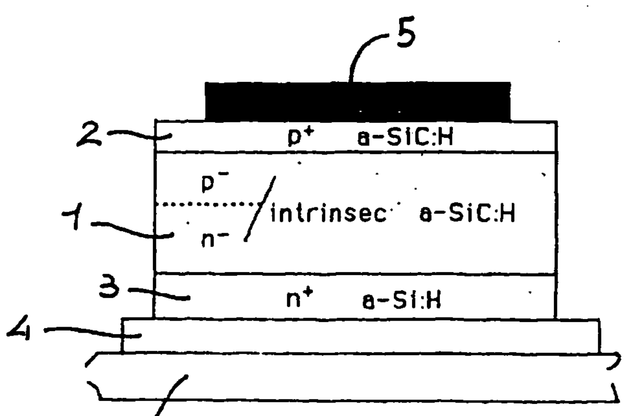

Fig. 1 b

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EUROPEAN SEARCH REPORT

Application Number
EP 96 83 0052

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	IEEE TRANSACTIONS ON ELECTRON DEVICES, vol. 39, no. 2, 1 February 1992, pages 292-296, XP000247206 FANG Y K: "AN AMORPHOUS SIC/SI HETEROJUNCTION P-I-N DIODE FOR LOW-NOISE AND HIGH-SENSITIVITY UV DETECTOR" * abstract * * page 293, column 1, line 5 - line 9 * * page 293, column 2, line 3 - line 6 * * page 294, column 1, line 9 - line 28 * * page 295, paragraph 4 *	1,2	H01L31/103 H01L25/04 H01L31/105
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A	IEEE PHOTONICS TECHNOLOGY LETTERS, vol. 6, no. 3, 3 March 1994, pages 412-414, XP000439722 OKAMURA M ET AL: "INFRARED PHOTODETECTION USING A-SI:H PHOTODIODE" * page 412, column 1, line 23 - line 33; figure 1 *	1-4	H01L
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P,Y	EP 0 682 375 A (UNI DEGLI STUDI DI ROMA LA SAP) 15 November 1995 * abstract; figures 1,2,10 *	3-7	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 January 1997	Visscher, E

CATEGORY OF CITED DOCUMENTS

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